

Temperature dependent local structure of $\text{NdFeAsO}_{1-x}\text{F}_x$ system using arsenic K -edge extended x-ray absorption fine structure

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Abstract

Local structure of $\text{NdFeAsO}_{1-x}\text{F}_x$ ($x=0.0, 0.05, 0.15$ and 0.18) high temperature iron pnictide superconductor system is studied using arsenic K -edge extended x-ray absorption fine structure measurements as a function of temperature. Fe-As bondlength shows only a weak temperature and F-substitution dependence, consistent with the strong covalent nature of this bond. The temperature dependence of the mean-square relative-displacements of the Fe-As bondlength are well described by the correlated-Einstein model for all the samples, but with different Einstein-temperatures for the superconducting and non-superconducting samples. The results indicate distinct local Fe-As lattice dynamics in the superconducting and non-superconducting iron-pnictide systems.

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I. INTRODUCTION

The role of structural topology in the magnetic and superconducting properties of the newly discovered iron-based superconductors (FeSC) is one of the active themes of investigation [1–3] focussing on finding the mechanisms of the unconventional superconductivity. Several studies have shown unprecedented sensitivity of Fermi surface topology to the anion (pnictogen or chalcogen) height above the Fe-plane in these materials. The anion height is seen to influence the density of states near the Fermi energy and influence the electron-pairing properties of the FeSC [4–10]. In addition, local structural studies have clearly pointed out the importance of the local order-disorder in the spacer layer in the FeSC [11, 12]. The structurally simplest systems among the FeSC, the $\text{FeTe}_{1-x}\text{Se}_x$, is found to have lower local structural symmetry than the average crystallographic symmetry, with the Se and Te occupying distinct sites [13, 14]. This local inhomogeneity is found to have a direct consequence on the electronic properties of the system [15]. All these point to the importance of the diverging local structure from the average one, putting the FeSC on the same platform of cuprates, revealing lattice anomalies and local inhomogeneities [16], closely related with the superconducting properties. Some recent EXAFS studies on F-doped LaFeAsO and SmFeAsO have shown a weak anomaly in the Fe-As bondlength fluctuations close to the superconducting transition [17, 18]. However, such anomalies are found to be much weaker, compared to those observed in the cuprates [16].

Here, we have used extended x-ray absorption fine structure (EXAFS), a fast and site-specific experimental tool [19, 20], to probe systematically the local structure of $\text{NdFeAsO}_{1-x}\text{F}_x$ oxypnictides as a function of temperature and charge density. Arsenic K -edge EXAFS has been used to retrieve direct information on the Fe-As bondlengths in superconducting ($x=0.15$ and 0.18) and non-superconducting ($x=0.0$ and 0.05) samples. The bondlengths show weak temperature and F-doping dependence, consistent with the strong covalent nature of the Fe-As bonds. The corresponding mean square relative displacements (MSRDs), well described by the correlated Einstein model, reveal different Einstein-temperatures (Θ_E) for the superconducting ($\Theta_E=348\pm12$ K) and non-superconducting ($\Theta_E=326\pm12$ K) samples. The superconducting sample with maximum T_c ($x = 0.18$) appears to show a weak temperature dependent anomaly in the Fe-As MSRDs. However, the anomaly is well within the experimental uncertainties, similar to case of $\text{SmFeAsO}_{0.931}\text{F}_{0.069}$.

These results indicate that there exists, distinct lattice dynamics in the superconducting and non-superconducting systems, albeit the differences are smaller.

II. EXPERIMENTAL METHODS

Temperature dependent x-ray absorption measurements were performed in transmission mode on powder samples of $\text{NdFeAsO}_{1-x}\text{F}_x$ ($x=0.0, 0.05, 0.15$ and 0.18 ; the x -values given corresponds to the nominal composition, the actual values are lower than the nominal values for higher x [21]), at the BM26A beamline [22] of the European synchrotron radiation facility, Grenoble (France). The synchrotron light emitted by a bending magnetic source was monochromatized by a double crystal $\text{Si}(111)$ monochromator. The samples, synthesized by conventional solid state reaction method [21], were characterized for their structural, magnetic and superconducting properties prior to the experimental run. While the samples $x=0.0$ and 0.05 are non-superconducting, showing tetragonal to orthorhombic structural phase transition, the samples with $x=0.15$ and 0.18 are superconducting with $T_c \sim 20$ K and ~ 40 K respectively, without any evidence of the structural phase transition [21]. For the temperature dependent measurements (15-300 K), a continuous flow He cryostat with a temperature control within an accuracy of ± 1 K was used. A minimum of two scans (with high signal to noise ratio) were measured at each temperature to make sure the reproducibility. Standard procedure was used to extract the EXAFS oscillations from the absorption spectrum [19, 20].

III. RESULTS AND DISCUSSIONS

Figure 1 shows Fourier transform (FT) magnitudes of the arsenic K -edge EXAFS oscillations (the insets show the EXAFS oscillations), measured on $\text{NdFeAsO}_{1-x}\text{F}_x$ (for $x=0.0, 0.05, 0.15$ and 0.18) samples, providing partial atomic distribution around the arsenic atoms. At room temperature, all the samples studied have tetragonal structure (space group $P4/nmm$) [21]. The $x=0.0$ and 0.05 samples show structural phase transition from tetragonal to orthorhombic phase below ~ 130 K [21]. There are four Fe atoms as the near neighbors of arsenic at a distance ~ 2.39 Å (main peak at ~ 2 Å). The next nearest neighbors are four Nd atoms at a distance ~ 3.28 Å and four oxygen atoms at a distance \sim

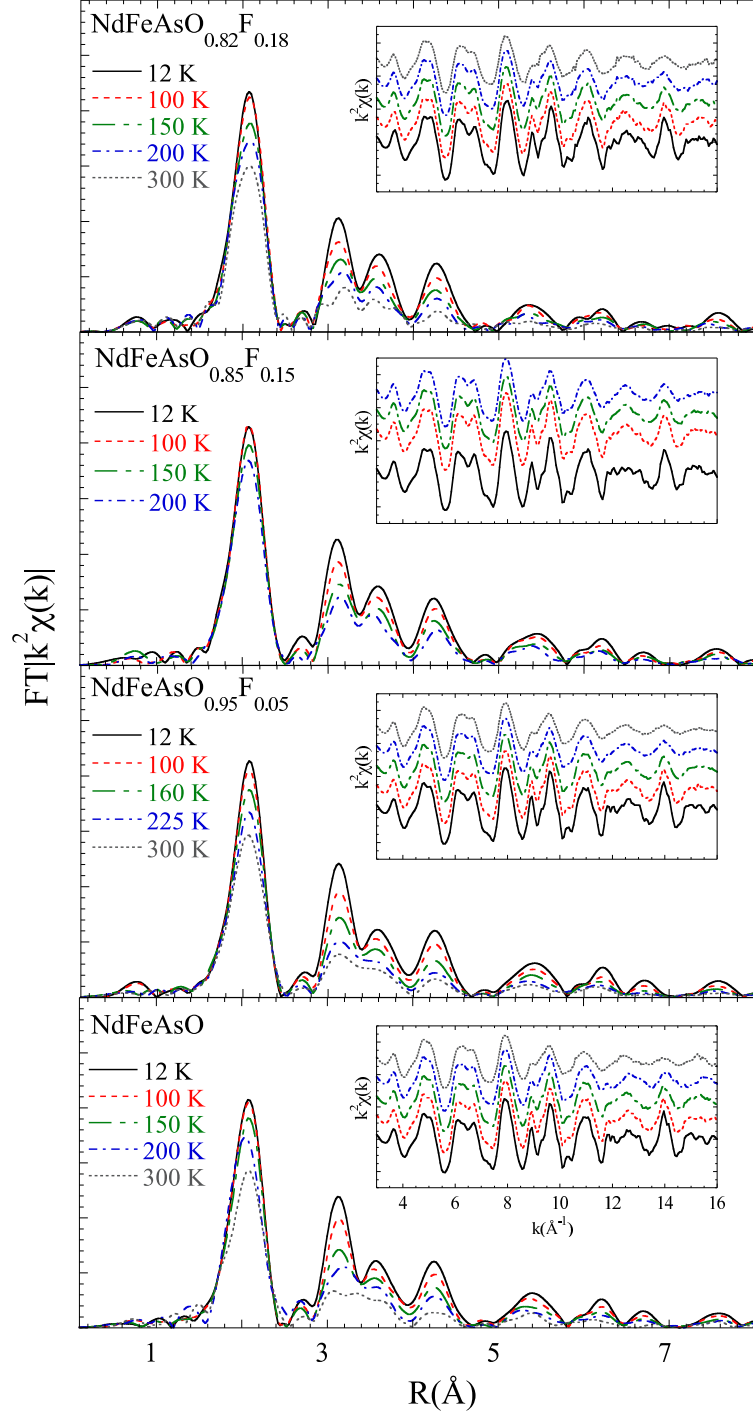


FIG. 1: Fourier transform (FT) magnitudes of the arsenic K -edge EXAFS oscillations for the $\text{NdFeAsO}_{1-x}\text{F}_x$ ($x=0.0, 0.05, 0.15$ and 0.18). Corresponding EXAFS oscillations are shown in the insets. The FTs are not corrected for the phase shifts, thus represent raw experimental data. A systematic temperature dependence is evident from the gradual change in the FT intensities.

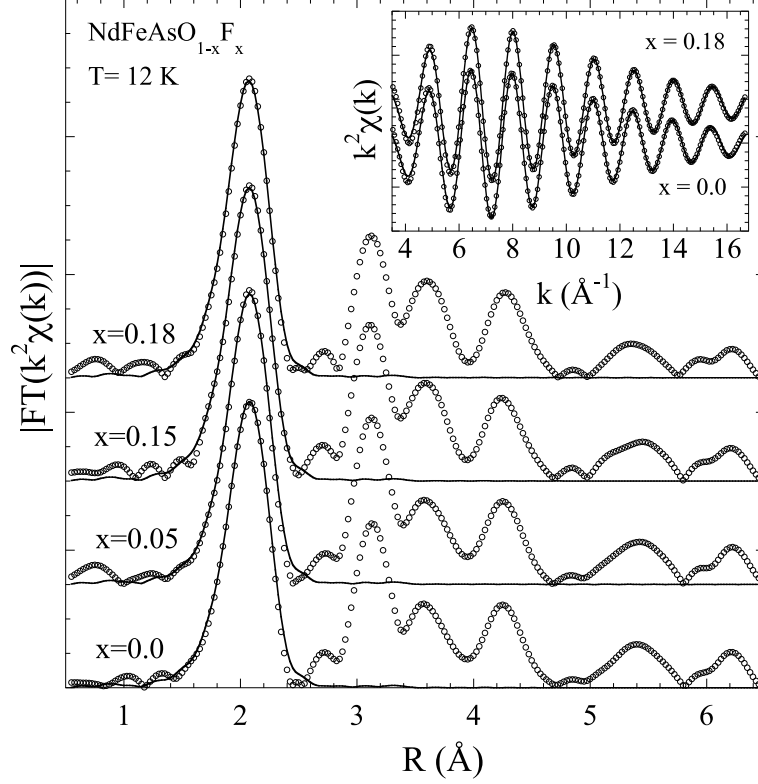


FIG. 2: Fourier transforms of the arsenic K -edge EXAFS oscillations measured (symbols) on $\text{NdFeAsO}_{1-x}\text{F}_x$ ($x=0.0, 0.05, 0.15$ and 0.18) at low temperature (12 K), together with a single shell fit (solid line). The filtered EXAFS oscillations corresponding to the first shell (As-Fe pairs) together with the model fits (solid lines) for $x=0.0$ and $x=0.18$ samples at 12 K are shown in the inset.

3.51 Å, followed by eight As atoms at ~ 3.9 Å. Contributions of these distant shells appear mixed, giving a multiple structured peak at $\sim 2.5\text{-}4.5$ Å (Fig. 1). Apparently, the atomic distribution around the arsenic is similar in all the samples, as evident from the FT as well the EXAFS oscillations.

In the $\text{NdFeAsO}_{1-x}\text{F}_x$ system, the arsenic atoms have the nearest neighbors as Fe atoms, and their contributions to the arsenic K -edge EXAFS is well separated from all other shell contributions. This makes the arsenic K -edge EXAFS data highly suitable for extracting quantitative information on the Fe-As bondlengths and the related mean square relative displacements (MSRDs). Here we have exploited this possibility and performed single shell model fits to the EXAFS oscillations due to the Fe-As bondlengths.

The EXAFS amplitude depends on several factors and is given by the following general

equation [19, 20]:

$$\chi(k) = \sum_i \frac{N_i S_0^2}{k R_i^2} f_i(k, R_i) e^{-\frac{2R_i}{\lambda}} e^{-2k^2 \sigma_i^2} \sin[2k R_i + \delta_i(k)]$$

where N_i is the number of neighboring atoms at a distance R_i , S_0^2 is the passive electrons reduction factor, $f_i(k, R_i)$ is the backscattering amplitude, λ is the photoelectron mean free path, δ_i is the phase shift, and σ_i^2 is the correlated Debye-Waller (DW) factor, measuring the mean square relative displacements (MSRDs) of the photoabsorber-backscatterer pairs. Apart from these variables, the photoelectron energy origin, E_0 , is another input needed for the modeling of the EXAFS. In the present case, we have used a single-shell EXAFS-modeling [19] to extract the Fe-As bond correlations. For such a single-shell analysis, we have used the WINXAS package [23], with backscattering amplitudes and phase shifts calculated using FEFF [24] with the crystal structure data from diffraction [21] as input. In the single-shell least-square fit, the number of independent data points, $N_{ind} \sim (2\Delta k \Delta R)/\pi$ [19] were about 13 ($\Delta k = 14 \text{ \AA}^{-1}$ ($k = 3-17 \text{ \AA}^{-1}$) and $\Delta R = 1.5 \text{ \AA}$), but, we used only two parameters, the radial distance R_i and the corresponding MSRD σ_i^2 , as the refinable variables, fixing all other parameters ($S_0^2 = 1$), to obtain reliable information on the Fe-As bond correlations. The uncertainties in the derived two parameters, R and σ^2 , were estimated by standard EXAFS method [20]. The canonical approach to error estimation is to determine the region around the best fit that contains the true value with a certain probability β . The projection of that volume onto an axis corresponding to a parameter gives the parameter errors, for a chosen value of β . In general this uncertainty is dependent on the experimental as well as EXAFS data extraction procedures, in addition to the uncertainties coming from the statistical χ^2 -procedure. In the present case, due to the adoption of identical experimental conditions and EXAFS data extraction procedures, the first kind of uncertainties are minimum. However, we have set the error bars on derived parameters, R and σ^2 , to two times the highest uncertainty estimated. This is to underline the fact that we are interested in discussing the relative changes rather than the absolute values of these parameters. Figure 2 shows the single shell model fit in the real and k -space at 12 K for samples with different x . Here it should be mentioned that the samples used in the present study are phase pure with the amount of impurities below the sensitivity of the x-ray diffraction. The main impurity phase present in the doped samples is NdOF phase, which showed a F-doping dependence [21]. However, in the present case, this impurity phase has no influence on the arsenic K -edge

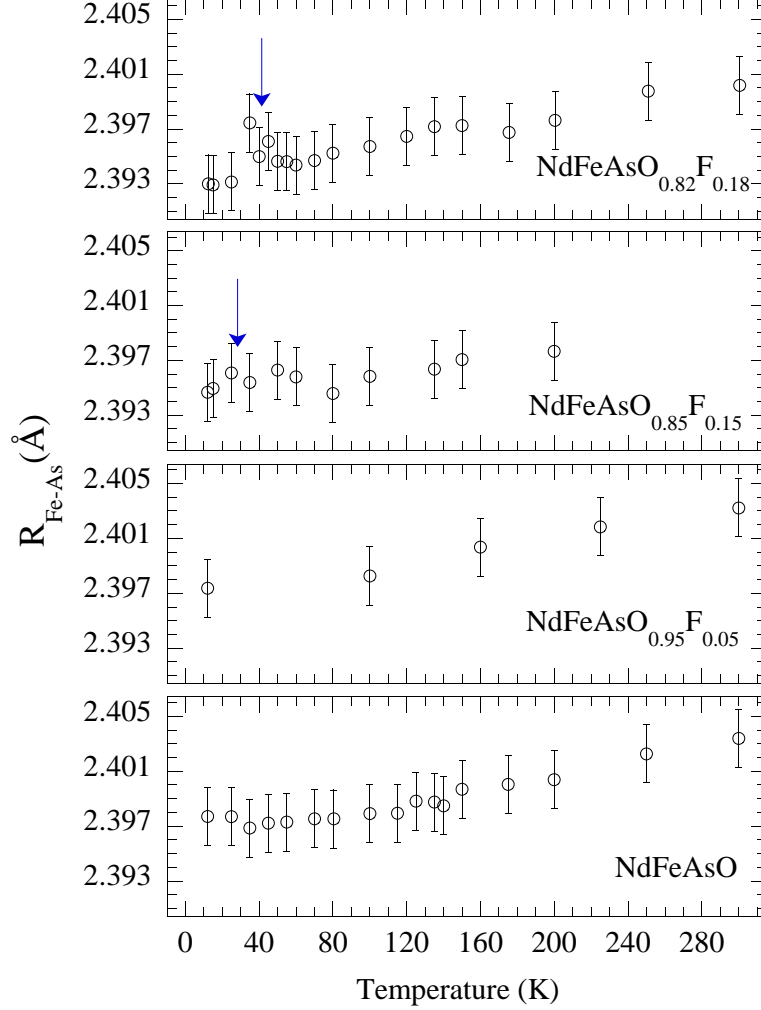


FIG. 3: Temperature dependence of the Fe-As bond distance for the $\text{NdFeAsO}_{1-x}\text{F}_x$ system. The Fe-As bond-length show only weak doping and temperature dependence, indicating covalent nature of the bond. However, there appears a small anomaly (arrow marks in the upper panels) in the superconducting samples close to the transition temperature, with no such changes evidenced in the non-superconducting compounds.

EXAFS data. The impurities which possibly can interfere with the present EXAFS results, like, the FeAs phases, NdAs phases were less than 1% [21], thus ruling out any contribution from such impurity phases in the data presented here.

Figure 3 shows temperature dependence of the Fe-As bond distances determined from the single shell analysis of the arsenic K -edge EXAFS data. The Fe-As distance in all the samples are very similar, around 2.39 Å. The over-all temperature dependence of the distance also looks very similar. However, one can notice a small change in the superconducting

samples somewhat close to the transition temperature, with no such changes evidenced in the parent compound. An earlier temperature dependent x-ray diffraction study on the $\text{NdFeAsO}_{0.85}$ superconductor has showed an abrupt change in the Fe-As distance around T_c [27]. Present results also show that the Fe-As distance tend to change near the T_c for the superconducting ($x=0.15, 0.18$) samples (Fig. 3 upper panels). But, we do not see significant changes in the Fe-As bondlengths or corresponding MSRD across the structural phase transition for the parent compound, which is consistent with earlier EXAFS studies on LaFeAsO [17, 28], SmFeAsO [18] and BaFe_2As_2 [29], showing no change in the Fe-As bondlength and corresponding MSRD across the structural phase transition. As shown in a recent diffraction study of the REFeAsO (RE stands for rare-earth) system, data from single crystals are important in for a better understanding of structural phase transition properties [25]. For example, a recent study on the NdFeAsO single crystal revealed two low-temperature phase transitions in addition to the tetragonal-to-orthorhombic transition at $T_S \sim 142$ K [26] indicating the importance of single crystals in revealing the intricate properties of FeSC. Naturally EXAFS studies using single crystals are also going to be important, in addition to the angular dependent local information provided by the polarization dependent EXAFS measurements [16].

Figure 4 shows mean square relative displacements (σ^2) of the Fe-As pair, describing distance-distance correlation function (correlated Debye Waller factors). The MSRD is a sum of temperature independent (σ_0^2) and temperature dependent terms [19], i.e.,

$$\sigma_{Fe-As}^2 = \sigma_0^2 + \sigma_{Fe-As}^2(T)$$

In several cases, the temperature dependent term can be described by the correlated Einstein-model [19, 20],

$$\sigma_{Fe-As}^2(T) = \frac{\hbar}{2\mu_{Fe-As}\omega_E} \coth\left(\frac{\hbar\omega_E}{2k_B T}\right),$$

where μ_{Fe-As} is the reduced mass of the Fe-As bond and ω_E is the Einstein-frequency. The related Einstein-temperature can be obtained from the expression $\Theta_E = \hbar\omega_E/k_B$. In the present case, temperature dependence of σ_{Fe-As}^2 is found to follow the correlated-Einstein model. Description of σ_{Fe-As}^2 using this model yield Θ_E values to be 348 ± 12 K and 326 ± 12 K respectively for the $x=0.18$ and the $x=0.0$ samples. Notice that the uncertainty in Θ_E given above are obtained from the least-square fit considering the error bars on the data

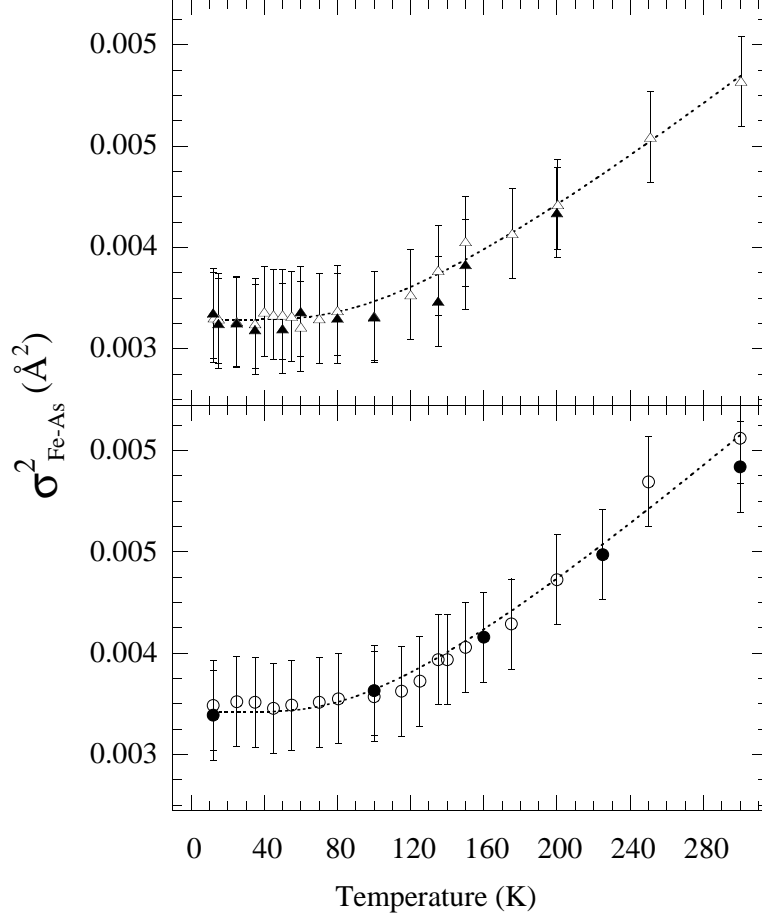


FIG. 4: Temperature dependence of the Fe-As MSD (symbols) for the $\text{NdFeAsO}_{1-x}\text{F}_x$ ($x=0.0, 0.05, 0.15$ and 0.18) system. Upper panel shows the data on the superconducting samples (open and filled symbols corresponds to $x=0.18$ and 0.15 samples respectively), while the lower panel shows the data on the non-superconducting samples (open and filled symbols corresponds to $x=0.0$ and 0.05 samples respectively). The dotted lines represent the correlated Einstein model fit to the data. The Einstein-temperatures, Θ_E , are 348 ± 12 K and 326 ± 12 K respectively for the superconducting ($x=0.18$) and non-superconducting ($x=0.0$) samples. The temperature independent σ_0^2 is found to have similar value (~ 0.00073) in both the cases.

points. The obtained Einstein-frequencies are in the range of phonon-frequencies observed in Raman studies for the modes involving arsenic and iron atoms [31, 32]. In addition, different Einstein frequencies (ω_E) indicate different local force constants ($k = \mu_{\text{Fe-As}} \omega_E^2$, where k is the effective force constant) for the Fe-As bonds in the superconducting and non-superconducting samples. The calculated local force constants for the Fe-As bonds are

~ 6.65 eV/Å² and ~ 5.85 eV/Å² respectively for the superconducting and non superconducting samples. Thus the Fe-As bondlength seems to get harder in the superconducting regime. This observation is an indication of non-negligible role of the lattice modes in the superconductivity of these materials.

Comparing the already available local structural data on different oxypnictides [17, 18, 28, 29, 33, 34] one can see that the Fe-As bond in these systems shows only little changes with doping and temperature. An EXAFS study on a series of oxypnictides [33] have shown that the Fe-As bondlength and the related MSRDs hardly show any change with the varying rare earth size, consistent with the strong covalent nature of the Fe-As bonds. On the other hand, earlier studies on F doped La-1111 [17] and Sm-1111 [18] compounds have shown presence of an anomaly in the temperature dependence of the Fe-As MSRDs. But these anomalies were seen to be very weak comparing to that observed for the cuprates [16]. Indeed another study on superconducting La-1111 system [28] did not indicate any such anomaly. Such anomalies were also not seen in the K doped Ba-122 system [29] and F doped Ce-1111 system [30]. From the results presented in Figure 4, for the F-doped Nd-1111 system, there is no evidence for a significant anomaly in the MSRD of Fe-As bonds associated with the superconducting transition. Here, we make an explicit comparison of the Fe-As MSRDs of the superconducting Sm-1111 and Nd-1111 samples to underline that the Fe-As MSRDs tend to change around the superconducting transition temperature, albeit the anomalies are indeed weak in compare to what has been seen in the copper oxide superconductors [16].

Figure 5 shows temperature dependence of the MSRDs of the Fe-As bond for the NdFeAsO, compared with that of the LaFeAsO [28], SmFeAsO [18] and BaFe₂As₂ [29]. In all the cases, the MSRD data are extracted from the arsenic *K*-edge EXAFS. Correlated-Einstein model fit to the data is also indicated in the figure (as dotted lines). From Fig. 5, it can be seen that the Fe-As MSRDs show almost identical temperature dependence for these different oxypnictide systems. Although the temperature dependence looks very similar, there seems to be a systematic change in the Einstein-temperature. The Θ_E values are respectively, 316 ± 5 K, 318 ± 10 K, 326 ± 12 K, and 328 ± 12 K for the LaFeAsO, BaFe₂As₂, NdFeAsO and SmFeAsO. There is a clear increase in the force-constant of the Fe-As bonds, with increasing RE size in the “1111” series. Optical studies using single crystals of the “1111” series reveal that the Fe-As stretching mode in these oxypnictides shows substantial hardening with the rare-earth size, being harder for the NdFeAsO and SmFeAsO showing

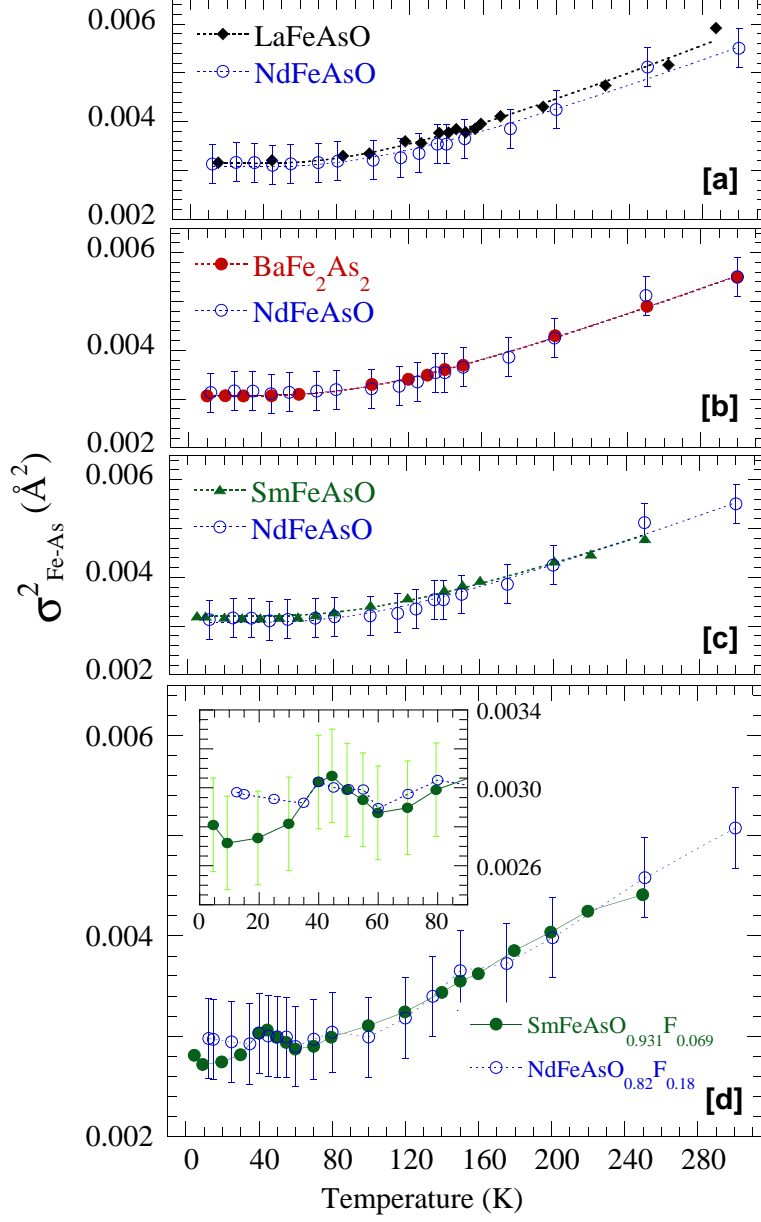


FIG. 5: Temperature dependence of the Fe-As MSRDS for the NdFeAsO system (open circles in all panels) is compared with that of the LaFeAsO [28] (filled diamonds (a)), SmFeAsO [18] (filled triangles, (b)) and the BaFe₂As₂ [29] (filled circles, (c)). For facilitating a better comparison, the LaFeAsO [28], BaFe₂As₂ [29] and SmFeAsO [18] data are scaled respectively by 0.0004, 0.0008 and 0.0017. Panel (d) presents the temperature dependence of the Fe-As MSRDS for the F doped superconducting Nd-1111 and Sm-1111 [18] (with the latter scaled by 0.0012). Overall temperature dependence of the two superconducting systems are identical. Inset in panel (d) shows a zoom around the superconducting transition temperature. The error-bars in the inset are identical as that given in Ref. [18].

higher T_c in compare to the LaFeAsO [35]. The E_u mode frequency for the BaFe₂As₂ [36] is also found to be similar to that of the “1111” series [35]. In the “1111” family, the changing rare-earth ionic size leads to a change in the pnictogen height above the Fe-plane [33] and thus a different interlayer atomic correlations [11, 12]. Local structural studies using atomic pair distribution function analysis on Ba_{1-x}K_xFe₂As₂ show that, although the changes in the Fe-As bonds are minimum, the FeAs₄ tetrahedra show a systematic change with K doping [34]. Indeed a small change in the pnictogen height is known to have significant effect on the electronic properties of the system through changing degeneracy between different Fe 3d bands (in particular between the $d_{x^2-y^2}$ and d_{xz}/d_{yz}), with a direct implication on the magnetic structure and superconductivity [8, 10]. Very recent photo-emission studies have showed this pnictogen height dependent changes in the electronic structure [37] confirming the importance of even very small local structural changes in determining the properties of the FeSCs.

To further enlighten possible anomaly around the superconducting transition temperature, we have made an explicit comparison between the temperature dependent Fe-As MSRDs for the F doped highest T_c Nd-1111 and Sm-1111 [18] superconductors (see, e.g., Fig. 5[d]). The inset in figure 5[d] is a zoomed view around T_c . The error-bars given here are identical as given in Ref. [18]. For the NdFeAsO_{0.82}F_{0.18} sample, there is a weak anomaly in the temperature dependence of the Fe-As MSRDs similar to that observed in the superconducting SmFeAsO_{0.931}F_{0.069} [18]. However, the anomaly is well within the experimental uncertainties. This situation is different from that of cuprates [16] where several measurements showed clear lattice anomalies associated with the superconducting transition. Although more experiments are needed, the weakness of the anomalies does not imply that lattice fluctuations have minor role in the Fe-based superconductors. Indeed, the an empirical relationship between the superconducting transition temperature and the FeAs₄ tetrahedra in FeSCs [4–6] clearly establishes the role of local lattice in the superconducting properties. Local structural studies also underline the same point [33, 34]. The increased force constant of the Fe-As bonds in the superconducting sample compared to the parent compound in the Nd-1111 system indicate the importance of lattice dynamics in determining the properties. Systematic changes in the Fe-As force constant within the different iron-pnictide compounds, as revealed by the present study, further support this.

IV. CONCLUSIONS

In conclusion, we have carried out systematic temperature-dependent local structural studies of the $\text{NdFeAsO}_{1-x}\text{F}_x$ ($x=0.0, 0.05, 0.15$ and 0.18) high temperature pnictide superconductor using arsenic K -edge EXAFS. In all the samples, the temperature dependence of the mean-square relative-displacements (MSRDs) of the Fe-As bonds are found to follow the correlated-Einstein model. However, the Einstein-frequency for the superconducting sample is higher than that of the parent compound, indicating a hardening of the Fe-As bond in the former compared to the latter. The over-all temperature dependence of the MSRDs of the Fe-As bond seems to be similar in the NdFeAsO , SmFeAsO , LaFeAsO and BaFe_2As_2 , but with a systematic variation of the corresponding force constants. The changes occurring in the FeAs_4 tetrahedra, together with the coupling between the active layer and the spacer layer, may account for the changes in properties of different iron oxypnictide superconductors.

Acknowledgments

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